

T-1

Mechanics of Materials & Equation-of-State

Liquid Dynamics Theory

Duane C. Wallace

Ever since the hard sphere model was invented by Enskog in 1922, the study of liquid dynamics has been focused on the mathematically intractable problem of the geometrical constraints of hard sphere motion. The study of physically-realistic liquids has been ignored, to the extent that there still does not exist a theory of the motion of atoms in a liquid. What is needed is a Hamiltonian, approximately solvable for its energy levels, a partition function which sums these energy levels, and a comparison of the corresponding theoretical free energy with the equilibrium thermodynamic properties of liquids. We have carried out this program for classical monatomic liquids. The theoretical development is based on two important experimental properties of elemental liquids, together with an analysis of the many-particle configuration space inhabited by the liquid state. The theory gives back an excellent account of the equilibrium properties of elemental liquids, and is capable of application to nonequilibrium processes.

The liquid state of an element has the same theoretical description, whether the liquid evolves from the crystal by the normal melting process, or by anomalous melting. However, since we are going to infer liquid properties from information on the melting process, it is essential to recognize the existence of these two melting categories. Here is a summary of our published findings on the melting of elements.

(a) In normal melting there is no significant change in the electronic structure as, for example, metal crystal to metal liquid. Experimental data for the entropy of melting at constant density lie in a very narrow range, with mean and variance given by $\Delta S = 0.80 \pm 0.10 Nk$, for N atoms. We have concluded that the liquid contains a universal disordering entropy of $0.80 Nk$, relative to the crystal.

(b) In anomalous melting, there is a significant change in the electronic structure, as for example polar crystal to metal liquid. The entropy of melting at constant density is much higher than the normal value, being $1.48 - 3.85 Nk$ for the anomalous elements we have analyzed, and apparently contains the normal contribution, plus an amount due mostly to the increase in potential energy in going to the new electronic structure.

Since practically all the experimental complications are exhibited by the relatively few anomalous melting elements, we explicitly omit those elements from the following data analysis.

The second important experimental property is the ion motional contribution C_I to the specific heat at constant volume. The nearly-universal behavior of the elements is $C_I \approx 3Nk$ for both crystal and liquid at melt. Since we know in general that C_I is $3Nk$ for $3N$ independent harmonic oscillators and, in particular,

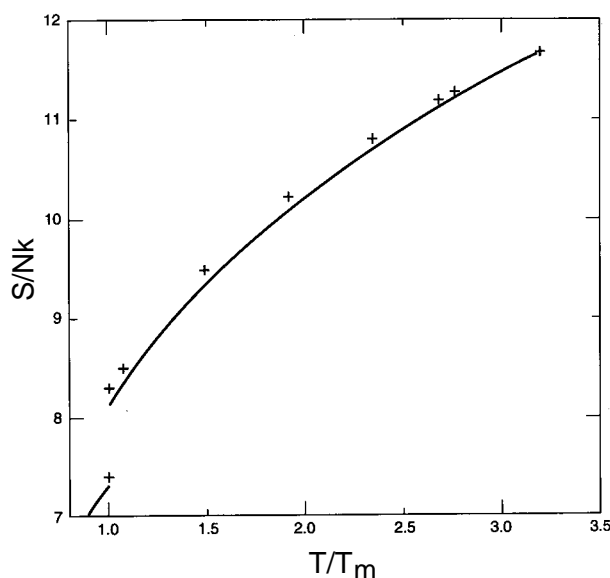


Figure 1: Entropy of mercury as function of temperature at constant density. Solid line is theory, including the nearly-free-electron contribution, and symbols are experimental data.

that lattice dynamics provides an excellent theory of ion motion in crystals in terms of $3N$ independent harmonic oscillators, we assume the ion motion in elemental liquids can be resolved to good approximation into $3N$ independent harmonic oscillators. This implies the ion motion is mainly confined within one or more nearly harmonic valleys in the potential energy surface.

The equilibrium configuration of ions at the bottom of a potential valley is called a “structure.” At the lowest energies lie a few crystalline structures, which are the basis of lattice dynamics theory. Structures without long range order are commonly called amorphous, and here it is necessary to divide these into two classes.

(a) Symmetric structures have a remnant of crystalline symmetry in their nearest-neighbor configurations, have a broad distribution of energies, and are relatively few in number.

(b) Random structures have a random distribution of nearest-neighbor configurations, they are by far the most numerous structures, and hence dominate the statistical mechanics of the liquid state. Furthermore, macroscopic averages such as the structure potential energy, and the set of normal mode frequencies, become the same for all random structures in the large- N limit.

The Hamiltonian describing the ion motion when the system is within the valley of any random structure is the sum of three terms: the structure potential energy, a set of $3N$ harmonic normal modes, and a correction term representing anharmonicity and the valley boundary condition. The anharmonic and boundary effects are small, and the partition function and free energy are easily evaluated in the quasiharmonic approximation. Now since the random structures all have the same potential energy, their valleys are all accessible to the liquid, and if their number is w^N , their multiplicity yields an entropy of $Nk \ln w$. We identify this as the universal disordering entropy of liquid relative to crystal, of magnitude $0.80 Nk$, hence we have $\ln w = 0.80$, and the number of random structures in configuration space is counted.

In the quasiharmonic approximation, thermodynamic functions of liquids are expressed by formulas without adjustable parameters. For all normal-melting elements for which we can evaluate the theoretical

expressions, agreement with experiment is excellent. The comparison of theory and experiment for the entropy of liquid mercury to high temperatures is shown in Figure 1.

Liquid dynamics is potentially as useful for liquids as is lattice dynamics for crystals, and we plan to continue the development of the present theory.